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STUDIES ON THE BLOCK COPOLYMERIZATION OF METHACRYLONITRILE AND HEXAFLUOROBUTYLMETHACRLATE USING PHENYLAZOTRIPHENYLMETHANE AS THERMAL INIFERTER

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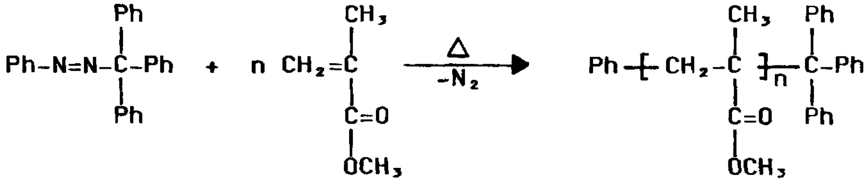
ABSTRACT

The iniferter technique was applied to synthesize a block copolymer of methacrylonitrile (MAN) and 2,3,3,4,4,4- hexafluorobutylmethacrylate (HFMA). Phenylazotriphenyl methane (PAT) was used as initiator for thermally initiated polymerization which proceeded via quasi-living radical mechanism. This was informed from the fact that yield and molecular weight ($\bar{M}n$) of the polymers increased with reaction time. The prepolymer obtained from one monomer was used as polymeric iniferter for the polymerization of the other monomer.This way block copolymers were obtained.

INTRODUCTION

Iniferter technique was extensively explored during the last decades for the preparation of block copolymers. In this concept, iniferters (initiator - transfer agent-terminator)are used to desing of the structure of polymer chain end in radical polymerization [1] . Dithiocarbamates were used as photoiniferters for the preparation of di- and tri-block copolymer [2] . Similarly, phenylazotriphenyl methane (PAT) [3] and tetraphenylsuccinodinitrile [4] were permitted to act as thermal iniferter. Several other types of iniferters were reported [5-9] . In the case of using PAT for the polymerization of methylmethacrylate, general reaction may be written as follows,

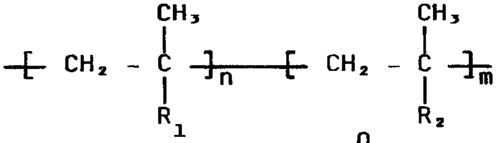


$$\text{Ph-N=N-}\underset{\text{Ph}}{\overset{\text{Ph}}{\text{C}}}\text{-Ph} + n\ \text{CH}_2\text{=}\underset{\underset{\text{OCH}_3}{|}}{\underset{\text{C=O}}{\overset{\text{CH}_3}{\text{C}}}} \xrightarrow[-N_2]{\Delta} \text{Ph}\left[\text{CH}_2\text{-}\underset{\underset{\text{OCH}_3}{|}}{\underset{\text{C=O}}{\overset{\text{CH}_3}{\text{C}}}}\right]_n\text{-}\underset{\text{Ph}}{\overset{\text{Ph}}{\text{C}}}\text{-Ph}$$

When the trityl terminated polymer was used as polymeric iniferter for the polymerization of styrene, the block copolymers were obtained.

Poly (methacrylonitrile) is a promising material in pozitive lithography due to high plasma etching resistance (10). The incorparation of fluorine atom leads to improved resist performance of polymethacrylates due to the higher radiation sensitivity (11). It seemed useful to prepare block copolymers with poly (methacrylonitrile) (PMAN) and poly (hexafluorobutylmethacrylate) (PHFMA) as components.

Therefore, it seemed appropriate to apply iniferter technique using PAT to prepare related copolymer.



$$-\!\!\left[CH_2-\overset{CH_3}{\underset{R_1}{C}} \right]_n\!\!-\!\!\left[CH_2-\overset{CH_3}{\underset{R_2}{C}} \right]_m\!\!-$$

PMAN = R_1: $-CN$, PHFMA = R_2: $-\overset{O}{\overset{\|}{C}}-O-CH_2-CHF-CF_2-CF_3$

EXPERIMENTAL

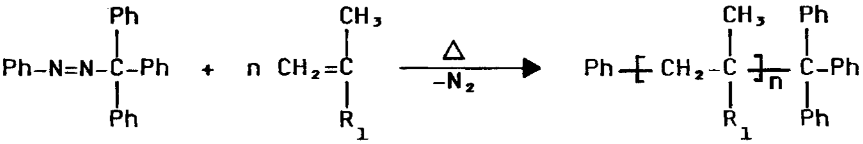
Monomers and solvents were purified by conventional drying and distillation procedures. PAT was synthesized according to decribed procedure (12).

Polymerizations of MAN in bulk or cyclohexanone solution were carried out in degassed and sealed tubes. The mixtures were then heated at 80 °C for a given time. Polymer formed was precipitated into excess n-hexane. For purification, the polymer was reprecipitated from acetone solutions with n-hexane. The block copolymerization was performed in a similar manner. The seperation of homo PHFMA was carried out by extracting with methanol.

Gel permeation chromatograms were obtained with the aid of a Knauer Instrument, model M64, using ethylmethyl ketone as eluent. The flow rate was 1 ml/min. Molecular weights were calculated on the bases of a calibration curve recorded with poly (methylmethacrylate) standard samples.

RESULTS AND DISCUSSION

PAT was found to initiate radical polymerization of MAN in the same way as reported for MMA polymerization[3].



$$Ph-N=N-\overset{Ph}{\underset{Ph}{C}}-Ph + n\ CH_2=\overset{CH_3}{\underset{R_1}{C}} \xrightarrow[-N_2]{\Delta} Ph-\!\!\left[CH_2-\overset{CH_3}{\underset{R_1}{C}} \right]_n\!\!-\overset{Ph}{\underset{Ph}{C}}-Ph$$

The observed time – conversion and time – molecular weight ($\bar{M}n$) relations are shown in Figures 1 and 2, respectively.

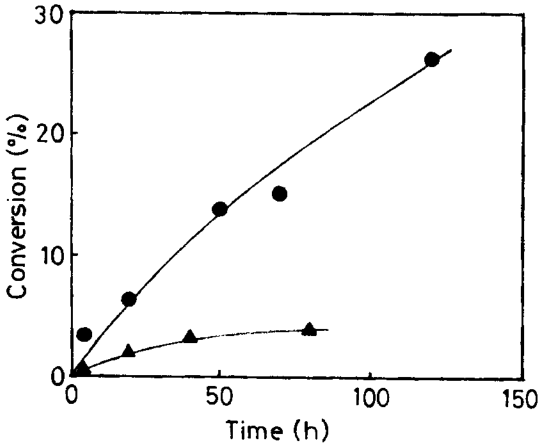


Figure.1: Time-conversion relations in polymerization of MAN, ▲: [PAT] = 3×10^{-3} M, 65°C in bulk, ■: [PAT] = 1×10^{-2} M, 80°C in cyclohexanone.

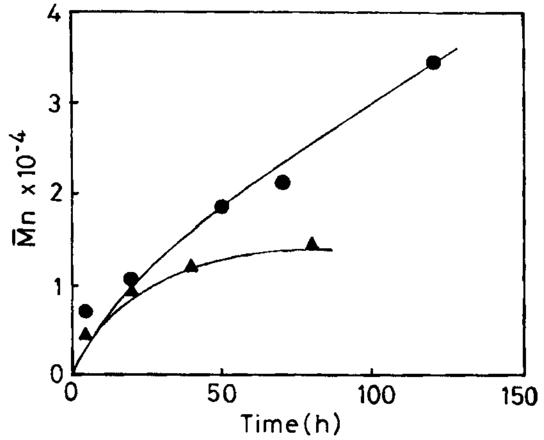


Figure.2: Time – molecular weight relations in polymerization of MAN ▲: [PAT] = 3×10^{-3} M, 65°C in bulk, ■: [PAT] = 1×10^{-2} M, 80°C in cyclo hexanone.

From this figures, it can be seen that both conversion and molecular weight of the polymers (PMAN) increased with reaction time. The $\overline{M}n$ values increased almost linearly with increasing conversion in both bulk and solution polymerization as can be seen from figure 3.

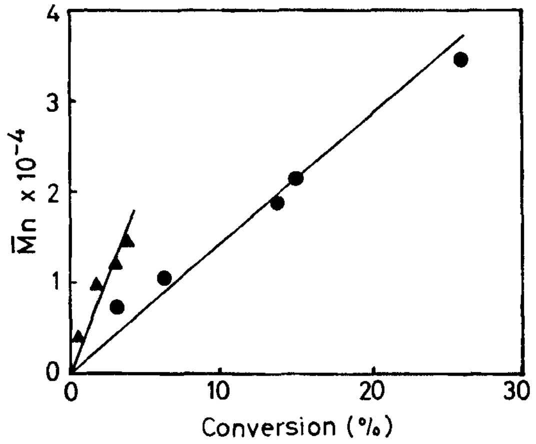
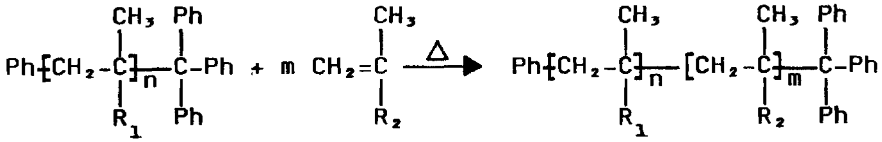


Figure.3: Conversion-Molecular weight relations in polymerization of MAN,
▲ : [PAT] = 3 x 10^{-3} M, 65°C in bulk,
■ : [PAT] = 1 x 10^{-2} M, 80°C in cyclo hexanone.

These findings are in accordance with the living radical polymerization concept, as proposed by Otsu et al[3], for the polymerization of MMA initiated by PAT. Further evidence for the proposed mechanism was obtained by the UV analysis of the resultant polymer. PMAN exhibits the UV absorption of trityl end group at λ_{max} = 230 nm. In order to synthesize block copolymers of MAN and HFMA, the polymerization of HFMA in the presence of PMAN were attempted. PMAN with trityl end groups are expected to initiate the polymerization of second monomer HFMA, in a manner similar to low molar mass iniferter, i.e. PAT. The general schema for the blocking process is as follows,



$$\mathrm{Ph}[\mathrm{CH_2}-\underset{R_1}{\overset{CH_3}{C}}]_n-\underset{Ph}{\overset{Ph}{C}}-\mathrm{Ph} + m\ \mathrm{CH_2}=\underset{R_2}{\overset{CH_3}{C}} \xrightarrow{\Delta} \mathrm{Ph}[\mathrm{CH_2}-\underset{R_1}{\overset{CH_3}{C}}]_n-[\mathrm{CH_2}-\underset{R_2}{\overset{CH_3}{C}}]_m-\underset{Ph}{\overset{Ph}{C}}-\mathrm{Ph}$$

Typical results obtained are shown in Table 1. The increase in total mass of polymer, Δm, reflects the formation of block copolymer.

TABLE 1
Block copolymerization of PMAN with HFMA[a)]

PMAN[b)] (g)	Time (h)	Yield (g)	HFMA Conv. (w %)	Δm [c)] (w %)	f_{PHFMA} [d)] (w %)
1	2.5	1.717	13.3	71.7	6.0
1	5.0	2.153	21.4	115.3	8.5
1	21.0	3.766	51.3	276.6	17.0
1	45.0	4.283	60.9	328.3	20.0

a) Polymerization condition : HFMA= 4 ml, cyclohexanone= 40 ml at 80°C,

b) Prepared by polymerization of MAN with PAT (10^{-2}M) in cyclohexanone at 80°C for 120 h,

c) $\Delta m = \frac{m_{final} - m_{start}}{m_{start}} \times 100$

d) Weight fraction of PHFMA in block copolymer (insoluble part in methanol), determined by IR spectra.

The fraction of PHFMA in the block copolymer depends linearly on the conversion as can be seen from figure 4.

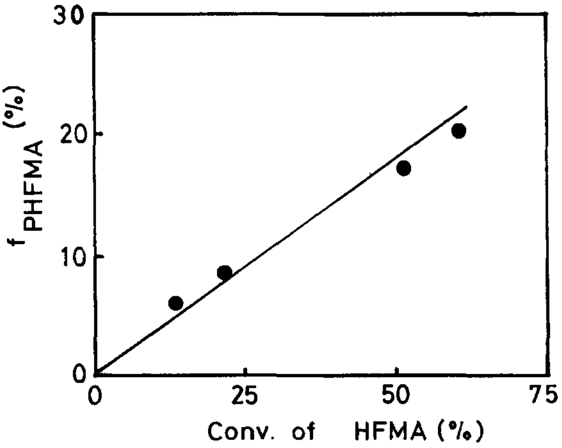


Figure.4: Conversion - content of PHFMA in block copolymer by polymerized PMAN with HFMA in cyclohexanone at 80°C.

Gel permeation chromatograms of prepoly (methacrylo nitrile) and block copolymer of methacrylonitrile and hexafluorobutylmethacrylate are presented in Figure 5. The new peak at higher molecular weight is ascribed to the block copolymer.

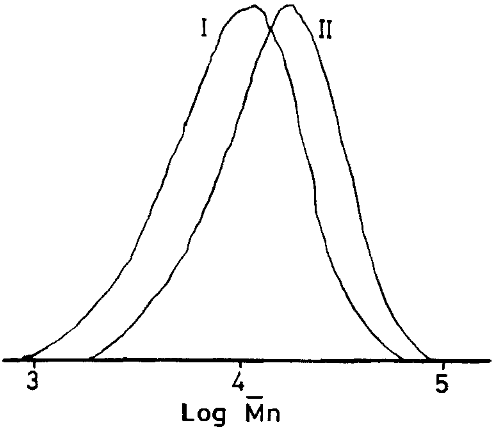


Figure.5: GPC curve of (I) prepoly (methacrylonitrile) obtained by using [PAT] = 10^{-2} M, MAN= 15 ml in cyclo hexanone (5 ml) at 80°C for 5 h, (II) block copolymer obtained by using PMAN= 0.25 g, HFMA= 2.5 ml in cyclohexanone (20 ml)at 80°C for 48h.

The seperation of homo PHFMA from the crude product was achieved by extracting with methanol which is non-solvent for PMAN. Further seperation was not possible due to the lack of availability of a solvent which is non-solvent for PHFMA but solvent for PMAN. Therefore, block copolymers may contain some unreacted PMAN. However this is not important as far as the use of the block copolymer in lithography is concerned. The corresponding two homo polymers are immiscible and they seperate into two phases and became practically useless due to the relatively weak adhesion between the two phases. On the other hand, homo PMAN is miscible with the block copolymer and forms a single phase.

The most .prominent advantage of this technique apparently consists in the introduction of new properties (high plasma etching and radiation sensitivity) which can be imparted to polymeric materials by block copolymerization of monomers of two different chemical nature.

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